C12 Determination of Free-Phase Conditions Using Ethylbenzene/Xylenes Ratios

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After attending this presentation, attendees will learn how to determine petroleum hydrocarbon free-phase conditions and identify source areas using ethylbenzene/xylenes ratios.

This presentation will impact the forensic community by providing a cost-effective method for determining site-specific free-phase screening levels for releases of gasoline and middle distillate petroleum products in soils that is based on soil types and contaminants present rather than the product that was released, is easily applied using typically available VOC data, and applicable to single and mixed overlapping release scenarios where ethylbenzene and xylenes are present. Additionally, mapping the EXR distribution at sites can identify release areas and soil migration pathways.

The presence of petroleum hydrocarbon (gasoline and middle distillates) free-phase conditions in soils is determined using an evaluation of xylenes and total volatile organic compound (VOC) concentrations to ethylbenzene/xylenes ratios (EXRs). Soil data exhibiting biodegradation from Michigan Leaking Underground Storage Tank (LUST) sites are presented that demonstrate EXR values correlating with free-phase conditions fall within a narrow range and thus are identified. Xylenes concentrations are shown to predict total VOC levels and those having EXR values at levels above the narrow range indicative for free-phase conditions are used to determine site- specific soil saturation concentration (Csat) screening levels.

"The Csat value is the concentration in soil at which the solubility limits of the soil pore water, the vapor phase limits of the soil pore air, and the absorptive limits of the soil particles have been reached. Csat is a theoretical threshold above which a free-phase liquid hazardous substance may exist. Free-Phase Liquid is a substance that is liquid in its natural state, is not dissolved in water and is at a concentration sufficient to allow it to flow and migrate in the environment separate from the influence of water." (Michigan Department of Environmental Quality (MDEQ) Operational Memorandum No. 1, Technical Support Document - Attachment 8, Part 201 Csat Concentrations, Part 213 Tier 1
Csat Concentrations, 2007).

"Bulk liquid hydrocarbons which coat soil particles are much less subject to environmental alteration, including biodegradation, than hydrocarbons at lower concentration uniformly dispersed in soil or dissolved in groundwater. This is because physical alteration processes mainly affect the interface and not the body of the bulk product. Biodegradation inside the body of the free product is extremely slow, because of the limitation of oxygen, water and nutrients (Hoag and Marley, 1986). It is likely that a hydrocarbon fuel in such conservative environments can survive for a very long time (over 20 years in some cases) with only minor changes in chemical composition." (www.dpra.com/index.cfm/m/160). Free-Phase Liquids represent long term sources of contamination because they will continue to supply contaminants to the environment and replace those which are transported away from the source area, are biodegraded, or removed through remediation (Alexander, 1999).

Gasoline, kerosene, diesel, and heating oil have composition ratios of ethylbenzene to xylenes of approximately 0.20±0.05. Upon a release, typically aerobic bacteria rapidly use the available oxygen and drive the release environment to an anaerobic condition. Ethylbenzene and xylenes are C_2 benzene compounds that have nearly identical boiling points, vapor pressures, water solubilities, and carbon-water sorption coefficients. Therefore, the major fate and transport mechanisms of evaporation, water-washing, contaminant velocity retardation, and mechanical dispersion affect ethylbenzene and xylenes alike. Anaerobic biodegradation will remove xylenes faster than ethylbenzene (Reinhard, Hopkins, and LeBron, 2005) and the EXRs will increase with time. An EXR of 0.25 or greater is an indication that anaerobic biodegradation is occurring. (Smith and DeWitt, 2006). Free product or free-phase conditions will act as continuing sources having extremely slow biodegradation resulting in continued elevated contaminant levels in soils and EXR values typically less than 0.25.

Ethylbenzene and xylenes soil data that exhibit anaerobic biodegradation decay are used to evaluate free-phase conditions and determine site-specific Csat screening levels. A graph is presented of the distribution of EXR values for over 100 cumulative soil samples that were observed from multiple LUST sites in Michigan, where xylenes concentrations were detected at levels above the MDEQ Tier 1 Csat screening level (150,000 µg/Kg). The Tier 1 Csat EXR distribution exhibits a general range of 0.07 to 0.24, extending down to 0.03 and up to 0.33, with a mean and median of 0.18. This observed range is consistent with the range predicted for petroleum products (0.20±0.05) and, therefore, is indicative of free-phase conditions.

Field examples are presented of 1) xylenes and total VOC soil concentrations versus EXR and 2) total VOCs versus xylenes for two LUST sites in Romulus (predominantly clay soils and gasoline, diesel, and

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kerosene potential sources) and Detroit (predominantly sand soils and gasoline and diesel potential sources), Michigan. Graphs are displayed for the combined clay/sand, clay, and sand soil types observed at each site. These field examples show that the higher contaminant levels, which include the MDEQ Tier 1 Csat values, fall within a narrow EXR range between 0.10 and 0.24. The steep onset and decline character of the distribution defines this narrow EXR range that is consistent with that predicted for petroleum products (0.20±0.05) and thus, is correlated with and identifies free-phase conditions. EXR values greater than approximately 0.25 are consistently associated with lower contaminant levels indicating free-phase conditions are not present at these locations and that anaerobic biodegradation is progressing.

The EXR data and map distribution for the Southfield, Michigan LUST site (gasoline, diesel, and fuel oil potential sources) is presented, which indicate a release area in the northeast portion of the site. Results for the predominantly clay soils show the typical character of the higher contaminant, free-phase EXR values falling within the narrow range generally between 0.15 and 0.26. The lower free-phase EXR values (0.15 to 0.26) are generally clustered in a former dispenser area in the northeast portion of the site indicating a historic dispenser release. The EXR data shows increasingly higher values to the southwest and south, where measurable biodegradation progresses at the lower contaminant levels. The extension of the lower EXR values to the south of the former dispensers and coincident with the former water and gas utilities in this area suggests a migration pathway was facilitated along these utility corridors.

Graphs of total VOCs versus xylenes show a direct linear correlation indicating that xylenes concentrations are a good predictor of total VOC concentrations. EXR values greater than typically 0.25 are associated with progressive biodegradation and lower contaminant levels, indicating free-phase conditions are not present at these locations. The xylenes concentrations for these data are used to statistically determine a site-specific Csat screening level. The site-specific xylenes Csat screening level is then used to calculate a site-specific total VOC Csat screening level, using the linear equation fit to the total VOCs versus xylene data. The site-specific total VOC Csat screening level is applicable for screening data to indicate free-phase conditions are not present where ethylbenzene and/or xylenes are below the laboratory detection limits or at lower contaminant levels within the elevated, narrow free-phase indicative EXR range below approximately 0.25.

In summary, the EXR method for determining site-specific Csat screening levels for releases of gasoline and middle distillate petroleum products in soils is based on the soil types and contaminants present rather than the product that was released, is easily applied using typically available VOC data, and applicable to single and mixed overlapping release scenarios where ethylbenzene and xylenes are present. Additionally, mapping the EXR distribution at sites can identify release areas and soil migration pathways.

Petroleum Hydrocarbons, Free Phase, Ethylbenzene and Xylenes

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